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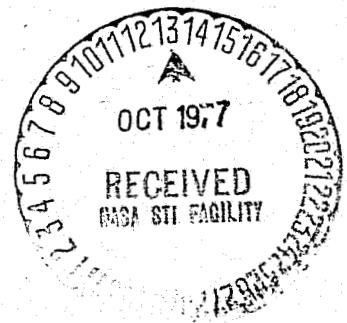
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National Aeronautics and
Space Administration

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California Institute of Technology
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Ananda K. Praturi
Ralph Lutwack
George Hsu

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California Institute of Technology
Pasadena, California 91103

PREFACE

The work described herein was performed by the Control and Energy Conversion Division of the Jet Propulsion Laboratory.

DEFINITION OF SYMBOLS

A	surface area of critical nuclei particles, cm^2
a'	inverse of the specific surface area of particles in fluidized beds, cm
C	concentration of gas phase, g mole/ cm^3
C_h	concentration of atomic hydrogen, g mole/ cm^3
\overline{C}_h	concentration of adsorbed atomic hydrogen, g mole/ cm^2
C_{h2}	concentration of molecular hydrogen, g mole/ cm^3
\overline{C}_{h2}	concentration of adsorbed molecular hydrogen, g mole/ cm^2
C_s	concentration of silicon vapor, g atom/ cm^3
\overline{C}_s	concentration of adsorbed silicon, g atom/ cm^2
C_{sb}	concentration of silane in bulk vapor phase, g mole/ cm^3
C_{si}	concentration of silane at the substrate surface, g mole/ cm^3
C_{ss}	concentration of silane, g mole/ cm^3
\overline{C}_{si}	concentration of adsorbed silane, g mole/ cm^2
C_v	concentration of vacant active sites, site/ cm^2
C_m	concentration of total active sites, site/ cm^2
d_p	particle diameter, cm
D_s	surface diffusion coefficient, cm^2/sec
D	diffusion coefficient, cm^2/sec
f	a constant, $1.554 \times 10^2 \text{ g}^{1/2} \text{ cal}^{1/2}/\text{cm}^2 \text{ atm sec}$
g^*	critical number of atoms (or molecules) in nucleus, g atoms
(g)	denotes gas phase
G	mass velocity, g/sec cm^2
J	rate of nucleation, no. of nuclei/ $\text{cm}^2 \text{ sec}$
J_D	mass transfer coefficient, dimensionless
k	Boltzman constant

k_a	specific reaction rate constant for adsorption
k_d'	specific reaction rate constant for desorption
k_d	specific reaction rate constant for reverse desorption
k_h	specific reaction rate constant for homogeneous pyrolysis
k_s	specific reaction rate constant for surface reaction
K	overall equilibrium constant for silicon CVD
K_c	mass transfer coefficient
K_h	equilibrium adsorption coefficient for atomic hydrogen
K_{h2}	equilibrium adsorption coefficient for molecular hydrogen
K_s	equilibrium adsorption coefficient for silicon vapor
K_{Si}	equilibrium adsorption coefficient for silane
m	molecular mass, g/mole
M	molecular weight g/g mole
n^*	concentration of critical nuclei, nuclei/cm ³
n_g^*	concentration of critical g-mers, g-mers/cm ³
n_g	concentration of g-mers, g-mers/cm ³
n_i	concentration of gas, g mole/cm ³
N_h	flux of hydrogen, g mole/sec cm ²
N_R	= $N_{Si}/(N_{Si} + N_h)$, flux ratio
N_{Si}	flux of silane, g mole/sec cm ²
\bar{N}_s	average concentration of adsorbed silicon, g mole/cm ²
N_s	equilibrium concentration of adsorbed silicon, g mole/cm ²
p	partial pressure of gas, atm
p'	equilibrium vapor pressure of gas, atm
P_{Si}	partial pressure of silane, atm
r^*	radius of the critical nucleus, cm
r_a	rate of adsorption, g mole/sec cm ²

r_d	rate of desorption, g mole/sec cm ²
r_h	rate of homogeneous pyrolysis, g mole/sec cm ³
r_{hp}	rate of heterogeneous pyrolysis, g mole/sec cm ³
r_m	rate of mass transfer, g mole/sec cm ³
r_o	overall rate of silicon CVD, g mole/sec cm ³
r_s	rate of surface reaction, g mole/sec cm ²
R	gas constant
Re_p	particle Reynolds number, dpG/u , dimensionless
(s)	denotes solid phase
S	supersaturation ratio, p/p'
Sh	Sherwood number, dimensionless
T	temperature, K
T_s	substrate temperature, K
V	reactor volume
\bar{X}	root mean square distance for diffusion before reevaporation (or desorption), cm
Z	film thickness for gas phase diffusion, cm
Z'	Zeldovich correction factor
α_c	condensation coefficient
Δf	vapor phase free energy change, cal/g
ΔF^*	critical free energy change for nucleation, cal/nucleus
ΔF_b	bulk free energy change for nucleation, cal/nucleus
ΔF_s	surface free energy change for nucleation, cal/nucleus
ΔF_g	free energy change for nucleation as a function of number of molecules in the nucleus, cal/g mole
ΔF_{sd}^*	Gibbs free energy change of activation for surface diffusion cal/g mole
ΔF_{des}^*	Gibbs free energy change of activation for desorption, cal/g mole

$\Delta F_{h_2}^\circ$	standard free energy of hydrogen molecules, cal/g mole
ΔF_S°	standard free energy of silicon, cal/g atom
ΔF_{Si}°	standard free energy of silane, cal/g mole
ΔF_R°	standard free energy change for reaction, cal/g mole
ΔH°	standard heat of formation, cal/g mole
ΔH_R°	standard heat of reaction, cal/g mole
ϵ	void fraction
ϵ_t	eddy diffusivity coefficient, cm^2/sec
$\bar{\epsilon}_t$	average eddy diffusivity coefficient, cm^2/sec
θ	contact angle, deg
$\bar{\lambda}$	mean spacing between ledges, cm
μ	viscosity coefficient, g/cm sec
ν	surface vibration frequency, sec^{-1}
ρ	density, g/cm^3
σ	specific surface free energy, erg/cm^2
σ_{S-v}	surface tension between substrate-vapor, erg/cm^2
σ_{C-S}	surface tension between condensate-substrate, erg/cm^2
σ_{C-v}	surface tension between condensate-vapor, erg/cm^2
ϕ	bulk flow correction factor
χ	functional relationship for contact-angle
Ω	molecular volume
ω	nuclei growth frequency, molecules/nucleus sec
$\bar{\omega}$	frequency factor for activated species

ABSTRACT

The four basic elements in the chemical vapor deposition (CVD) of silicon from silane are mass transport of silane, pyrolysis of silane, nucleation of silicon and silicon crystal growth. These four elements are analytically treated from a kinetic standpoint. Rate expressions that describe the various conceivable steps involved in the chemical vapor deposition of silicon are derived from elementary principles. Applications of the rate expressions for (1) modeling and the simulation of the silicon CVD process and (2) the analysis of experimental data on silicon CVD are discussed. The lack of an experimentally established mechanism of the silicon CVD process and established values for various constants involved in the rate expressions is the major impediment to the modeling of the CVD process. Experimental data are needed to determine the equilibrium adsorption coefficients for silane, hydrogen and silicon vapor and the activation energies and frequency factors for the various rate processes involved in the silicon CVD.

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SECTION I

INTRODUCTION

The Low-Cost Silicon Solar Array (LSSA) project sponsored at JPL by ERDA has the responsibility for developing the technology and the production capability for economically practical solar photovoltaic electricity generating plants. The objective is the achievement of a generating capacity of 500 megawatts peak at a cost of \$500 per kW by 1985. The program of LSSA is divided into four technology tasks, each of which has the responsibility for advancing a particular technical area so as to achieve the production and cost goals. The first of these tasks is the Silicon Material Task, for which the 1986 objective is to reduce the price of Si material, suitable for the fabrication of solar cells having satisfactory performance, from the present price of about \$65/kg (for semiconductor grade Si) to less than \$10/kg.

To achieve the price objective of the Si Material Task, new areas of chemical processing and solar cell technology must be studied and developed, since no modification of the basic processes presently used commercially will lead to the attainment of the \$10/kg price. The inability of the present commercial process to meet the task objective is revealed from a consideration of the features of this process. The first step is the reaction of metallurgical grade Si, having a purity of about 98.5%, with HCl in a fluidized bed reactor to yield the intermediate SiHCl_3 in a mixture of chlorinated silanes. After chemical treatment and fractional distillation to obtain very pure SiHCl_3 , semiconductor grade Si is produced by chemical vapor deposition resulting from the H_2 reduction of SiHCl_3 . This process to produce extremely pure Si is costly and energy-intensive, the final deposition consuming an estimated 385 kWh/kg Si product.

Several different chemical processes are being investigated under JPL contracts in the task program. A contract with Union Carbide involves the hydrogenation of SiCl_4 to SiHCl_3 in a fluidized bed as well as a process for the deposition of Si from SiH_4 in another fluidized bed.

To support the developments in silicon production, the task program includes an in-house JPL subtask for supporting studies of silicon production as well as a subtask for consultation in this area by Professors O. Levenspiel and T. Fitzgerald of Oregon State University. The in-house program consists of efforts in modeling of the deposition of Si in a fluidized bed reactor, experimental studies of SiH_4 pyrolysis and fine particle fluidization, and thermodynamic and chemical engineering analysis of the reactions in the fluidized process for silicon production. The initial phase of the effort in analysis of silicon chemical vapor deposition is described in this report.

The finite amount of available fossil fuels and the continually increasing energy requirements of mankind dictate the need for the development of alternate energy sources. Solar energy is one energy source that is abundantly available and can be harnessed by silicon solar cells to generate electric power. The production of polycrystalline

silicon by the pyrolysis of silane is a promising method for reducing the present-day high cost of silicon material suitable for silicon cells. Although the pyrolysis of silane has been extensively studied in connection with epitaxial growth of single-crystal silicon films, the mechanisms of silicon deposition in fluidized bed and free space reactors are little understood. The deposition process consists of several physical and chemical steps. The controlling step will depend on the reactor temperature and silane concentration. It is the purpose of this paper to establish the thermodynamic feasibility of the overall pyrolysis reaction and to develop rate expressions for the various individual steps of the deposition process. Rate expressions for the heterogeneous reaction kinetics of silane pyrolysis will be developed in the fashion of Hougen and Watson's treatment of Langmuir-Hinshelwood theory. Excellent accounts of this type of analysis can be found in Hougen and Watson (Reference 1-1) and Smith (Reference 1-2). Hirth and Pound (Reference 1-3) and Powell et al. (Reference 1-4) are the references used most in developing the kinetic expressions for nucleation and growth of silicon crystals.

Experimental data on the pyrolysis of silane have been reported by many investigators (References 1-5 through 1-9) usually in the form of Arrhenius equations. Kinetic parameters (activation energy and frequency factor) are studied for the calculation of the specific reaction rate constants for the conversion of silane or growth rate of silicon crystals. Different experimental conditions (temperature, pressure, concentrations, flow rates, and reactor geometry) have been used, and hence different overall kinetic constants for the pyrolysis of silane have been reported. These differences are generally attributed to the differences in the mechanisms of the CVD process under different experimental conditions, although the exact mechanism has never been proved.

Experimental evidence leads to some general conclusions about silane pyrolysis: the reaction is predominantly homogeneous at low temperatures (300-500°C) and is predominantly heterogeneous at higher temperatures (500-1200°C). The heterogeneous reaction is a diffusion limited process above 1000°C. The crystal structure of deposited silicon is a strong function of substrate temperature. If the reaction rate constants and expressions are known for all the individual steps in all possible mechanism sequences, it will be invaluable in the calculation of the overall conversion or growth rate for specified experimental conditions.

Development of rigorous rate expressions is the essential first step in this direction. In the present analysis, no assumptions are made as to the mechanism of the silicon CVD process, and rate expressions are derived for every conceivable elementary step (within the limits of reason). It is hoped that the present analysis will provide analytical expressions for modeling of the silicon CVD process and provide a sound theoretical basis for future experimental research on silicon CVD.

SECTION II

THERMODYNAMICS OF SILANE PYROLYSIS

There are two powerful tools in thermodynamics for the analysis of any chemical reaction, viz: the heat of reaction and the free energy change for the reaction. These two quantitative measures determine the feasibility of the reaction, the maximum extent of conversion and energy requirements for the process. The heat of reaction and free energy of reaction can be calculated from the heats of formation and standard free energies of the reactants and products by the following relations:

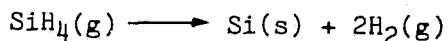
$$\text{heat of reaction } (\Delta H^\circ)_R = \text{heat of formation of products } (\Delta H^\circ) - \text{heat of formation of reactants } (\Delta H^\circ)$$

$$\begin{array}{ccccccc} \text{standard free} & & \text{standard free} & & \text{standard free} & & \text{standard free} \\ \text{energy of} & = & \text{energy of} & + & \text{energy of} & - & \text{energy of} \\ \text{reaction } (\Delta F^\circ)_R & & \text{silicon } (\Delta F^\circ)_S & & \text{hydrogen } (2\Delta F^\circ_{H_2}) & & \text{silane } (\Delta F^\circ)_{Si} \end{array}$$

The reaction equilibrium constant can be obtained from the expression

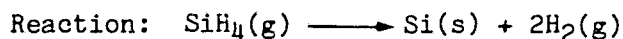
$$(\Delta F^\circ)_R = -RT \ln k$$

The overall reaction for silane pyrolysis can be written as



The standard free energy change, equilibrium constant and heat of reaction have been calculated for the temperature range 100 - 1600 K and are tabulated in Table 2-1. As can be observed from the data in Table 2-1, the pyrolysis of silane is exothermic and thermodynamically feasible in the temperature range 100 - 1600 K. The high values of the equilibrium constant, especially at higher temperatures, indicate almost 100% conversion, hence the irreversible nature of the reaction. Thus the thermodynamic analysis has shown that pyrolysis of silane is an irreversible and exothermic reaction.

Table 2-1. Standard Free Energy Change, Equilibrium Constant, and Heat of Reaction



units of free energy change and heat of reaction: cal/mole

Temp, K	$\Delta F_{\text{Si}}^{\circ}$	$\Delta F_{\text{S}}^{\circ}$	$\Delta F_{2\text{H}_2}^{\circ}$	$(-\Delta F_{\text{R}}^{\circ})$	ln K	$-\Delta H_{\text{R}}^{\circ}$
100	3164.4	27.9	3359.6	223.1	+1.1277	10097.7
200	7433.1	212.2	8685	1464.1	+3.6841	9311.1
298.15	12056.4	571.8	14561.6	3077.0	+5.1033	8634.9
300	12146.9	580.2	14678.0	3111.3	5.2189	7800.0
400	17206.6	1108.3	21138.4	5040.1	6.3407	7016.6
500	22574.5	1769.6	27949.4	7144.5	+7.1905	6394.6
600	28225.6	2544.0	35042.2	9360.6	7.8507	5917.9
700	34139.4	3415.9	42371.0	11647.5	8.3732	5569.7
800	40298.4	4374.0	49900.6	13976.2	8.7913	5330.1
900	46686.8	5407.5	57606.2	16326.9	9.1289	5177.2
1000	53290.4	6510.8	65469.4	18689.8	+9.4050	5091.9
1100	60096.1	7677.7	73482.8	21064.4	9.6364	5057.7
1200	67092.1	8903.3	81626.4	23437.6	9.8285	5060.5
1300	74267.6	10183.6	89891.8	25807.8	9.9900	5088.0
1400	81612.7	11515.4	98280.4	28183.1	10.1302	5132.2
1500	89118.2	12893.5	106770.8	30546.1	10.2476	5184.5
1600	96776.0	14318.9	115362.8	32905.7	10.3492	5240.7

Heat of formation and free energy data are from McBride, Heimel, Ehlers and Gordon, Thermodynamic Properties to 6000°K for 210 Substances Involving the First 18 Elements, NASA SP-3001, 1963.

SECTION III

KINETICS OF SILICON CVD

The overall chemical vapor deposition process consists of several physical and chemical steps. All the possible steps are illustrated in Figure 3-1. The exact path of the deposition mechanism depends on the temperatures of the vapor phase and substrate and silane concentrations.

The conceivable elementary steps* involved in silicon CVD are:

- (R₁) homogeneous pyrolysis of silane
- (R₂) homogeneous nucleation of silicon vapor
- (R₃) mass transport of silane gas to the substrate surface
- (R₄) mass transport of hydrogen away from the substrate surface
- (R₅) heterogeneous pyrolysis of silane adsorbed directly on nuclei
- (R₆) adsorption of silane on substrate surface
- (R₇) adsorption of silicon vapor on substrate surface
- (R₈) desorption of hydrogen from substrate surface

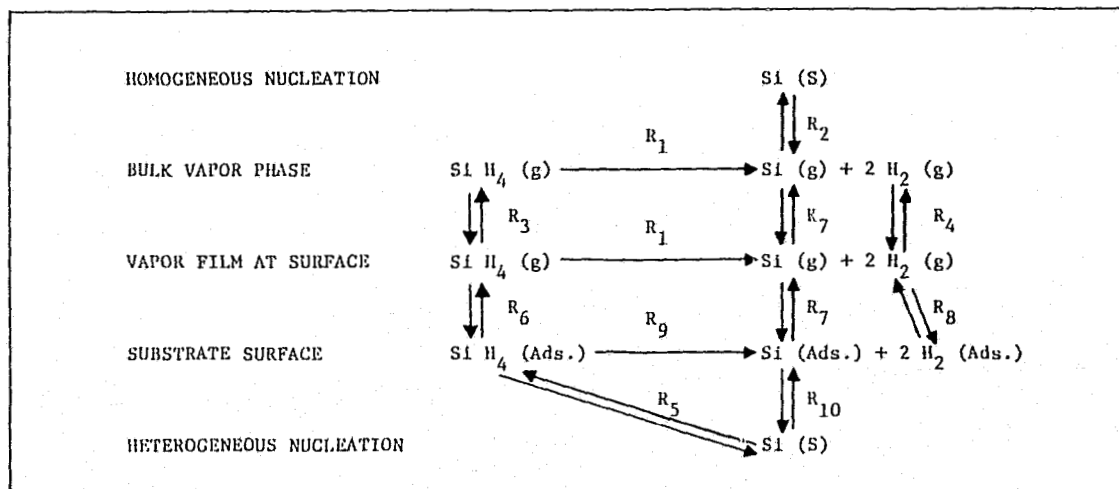


Figure 3-1. Schematic of Silane Pyrolysis

*These are the steps that are assumed to prevail, as the exact mechanisms of silicon CVD are not known.

(R₉) heterogeneous pyrolysis of silane adsorbed on substrate surface

(R₁₀) heterogeneous nucleation of adsorbed silicon

These elementary steps can be conveniently grouped into six categories: (1) mass transport of silane and hydrogen, (2) homogeneous pyrolysis of silane, (3) homogeneous nucleation of silicon, (4) heterogeneous pyrolysis of silane, (5) heterogeneous nucleation of silicon, and (6) silicon crystal growth. The actual mechanism of silicon CVD will consist of three or more of these six categories. Kinetic rate expressions for each of these steps will now be developed.

SECTION IV

MASS TRANSPORT

The diffusion of the reactant (silane) to the substrate surface (step R_3) and the diffusion of the product (hydrogen) away from the substrate surface (step R_4) are the important mass transport processes involved in the chemical vapor deposition of silicon from silane. The rates of R_3 or R_4 are not independent of each other and are dependent on the stoichiometry of the pyrolysis reaction. In the absence of equilibrium limitations, diffusion can be the limiting process in the CVD of silicon at high temperatures. In fact, many investigators of silicon epitaxy reported the process to be diffusion-limited. In such instances the reaction kinetics will be extremely fast and the overall rate of CVD can be obtained from a knowledge of the mass transport rates. The rate expressions for mass transport in flow reactors can be written by using the Stephen-Maxwell relation as;

$$N_{Si} = -(D + \epsilon_t) \frac{dC_{ss}}{dz} + \frac{C_{ss}}{C} (N_{Si} + N_h) \quad (1)$$

where N_{Si} is the flux of silane, D is the binary diffusion coefficient, ϵ_t is the eddy diffusivity coefficient, C_{ss} is the concentration of silane, C is the concentration of total gas phase, N_h is the flux of hydrogen and Z is the diffusion path length. Molecular diffusion is accounted for by D , and ϵ_t is an analogous eddy diffusivity to account for mass transport by turbulent convection. Eddy diffusivity is a function of distance from the surface, and this relationship is not generally known. Thus an average constant eddy diffusivity $\bar{\epsilon}_t$ is used for integration of Eq. (1) from bulk silane concentration (C_{sb}) to the silane concentration at the surface (C_{si}). The result of integration is:

$$N_{Si} = \frac{N_{Si}}{N_{Si} + N_h} \left(\frac{D + \bar{\epsilon}_t}{Z} \right) \ln \left\{ \frac{\left(\frac{N_{Si}}{N_{Si} + N_h} \right) - \left(\frac{C_{si}}{C} \right)}{\left(\frac{N_s}{N_{Si} + N_h} \right) - \left(\frac{C_{sb}}{C} \right)} \right\} \quad (2)$$

The value of Z , the diffusion path is not generally known and, hence the term

$$\left(\frac{D + \bar{\epsilon}_t}{Z} \right)$$

will be replaced by one variable, K_c , called a mass transfer coefficient. Equation (2) can be simplified by defining N_R and ϕ :

$$N_R = \frac{N_{Si}}{N_{Si} + N_h} \quad (3)$$

$$\phi = \frac{\left(N_R - \frac{C_{ss}}{C}\right) LM}{N_R} \quad (4)$$

with LM denoting logarithmic mean. For silane pyrolysis, $2N_{Si} = N_h$ by reaction stoichiometry and hence $N_R = -1$ and ϕ becomes:

$$\phi = \frac{\frac{C_{Si}}{C} - \frac{C_{Sb}}{C}}{\ln \left(\frac{1 + \frac{C_{Si}}{C}}{1 + \frac{C_{Sb}}{C}} \right)} \quad (5)$$

Equation (2) can now be reduced to a more familiar form of mass transfer equations, where r_m is the rate of mass transfer per unit reactor volume and a' is the inverse of the specific surface area of particles in the reactor.

$$r_m = \frac{K_c}{\phi} a' (C_{Sb} - C_{Si}) \quad (6)$$

But, as shown in Eq. (5), ϕ is a function of C_{Si} and C_{Sb} and cannot be included in the mass transfer coefficient. Substituting the value of ϕ from Eq. (5) in Eq. (6), the rate of mass transfer in silane pyrolysis reactors can be expressed as

$$r_m = k_c a' C \ln \left[\frac{1 + \frac{C_{Sb}}{C}}{1 + \frac{C_{Si}}{C}} \right] \quad (7)$$

For fluidized bed reactor systems the value of a' is expressed as

$$a' = \frac{6(1 - \epsilon)}{d_p},$$

where ϵ is the void fraction in the fluidized bed and d_p is the diameter of the particles in the reactor. The value of K_c can be obtained from empirical correlations. However, as Geankoplis (Reference 4-1) points out, care should be exercised in using these correlations, as some of the experiments were not conducted with $\phi = 1$. In such instances, the value of ϕ for the experimental conditions used in developing the correlations should be calculated and the true value of K_c obtained therefrom.

If the mass transport is the rate-limiting step in the silicon CVD process, i.e., the mass transport is the slowest step, the concentration of silane at the substrate can be assumed to be zero ($C_{Si} = 0$). Then, the rate of silicon CVD process can be determined from Eq. (7).

$$r_0 = K_c a' c \ln \left(1 + \frac{C_{sb}}{C} \right) \quad (8)$$

SECTION V

HETEROGENEOUS PYROLYSIS

The traditional approach to the analysis of heterogeneous kinetics, utilizing Langmuir's theory of adsorption and Hirschelwood's theory of surface reactions, was developed in detail by Hougen and Watson (Reference 1-1). The major assumptions made in this approach are (1) the reaction surface is energetically uniform, i.e., all the active centers have the same activity for adsorption; (2) the amount adsorbed has no effect on the rate of adsorption per site; i.e., there is no interaction between adsorbed molecules; (3) all the adsorption occurs by the same mechanism and each adsorbed complex has the same structure; (4) the extent of adsorption is less than one complete monomolecular layer on the surface; (5) the total number of active sites is constant; and (6) one of the steps in the process is usually controlling and the rest occur at equilibrium.

The three steps involved in heterogeneous decomposition of silane are adsorption of silane on the silicon substrate (R_6), surface reaction of silane (R_9), and desorption of hydrogen (R_8). Rate expressions for the three steps are derived by the Hougen-Watson procedure and included in Table 5-1. Rate equations for the surface reaction and hydrogen desorption are different for the different mechanisms of hydrogen adsorption (molecular, atomic or none). Stoichiometric equations and equilibrium concentrations of adsorbed species are also included in Table 5-1. Overall rate expressions for heterogeneous pyrolysis of silane can easily be derived if it is assumed that one of the steps is rate controlling and the rest occur at equilibrium. One useful relation in deriving the overall rates is Eq. (9), in which ' C_m ' represents the concentration of total active sites, ' C ' represents the concentration of vacant sites, and \bar{C}_{si} , \bar{C}_h , and \bar{C}_s represent concentrations of adsorbed silane, hydrogen and silicon:

$$C_m = \bar{C}_v + \bar{C}_{si} + \bar{C}_h + C_s \quad (9)$$

The overall rates (r_{hp}) of heterogeneous pyrolysis of silane are derived using Eq. (9) and rate equations and equilibrium concentrations given in Table 5-1. Equations (10) through (17) are the rate equations derived with one step assumed as the controlling step.

Silane adsorption controlling, with molecular hydrogen adsorption:

$$r_{hp} = \frac{k_a C_m}{1 + K_{h2} C_{h2}} C_{si} \quad (10)$$

Table 5-1. Rate Expressions for Heterogeneous Pyrolysis of Silane

Controlling Step	Hydrogen Adsorption Mode		
	Molecular	Atomic	None
Adsorption of silane	$\text{SiH}_4(\text{g}) + \text{X} \longrightarrow \text{SiH}_4 \cdot \text{X}$ $r_a = k_a \left(C_{\text{Si}} C_v - \frac{\bar{C}_{\text{Si}}}{K_{\text{Si}}} \right)$ $(\bar{C}_{\text{Si}})_{\text{eq.}} = K_{\text{Si}} C_{\text{Si}} C_v$	$\text{SiH}_4(\text{g}) + \text{X} \longrightarrow \text{SiH}_4 \cdot \text{X}$ $r_a = k_a \left(C_{\text{Si}} C_v - \frac{\bar{C}_{\text{Si}}}{K_{\text{Si}}} \right)$ $(\bar{C}_{\text{Si}})_{\text{eq.}} = K_{\text{Si}} C_{\text{Si}} C_v$	$\text{SiH}_4(\text{g}) + \text{X} \longrightarrow \text{SiH}_4 \cdot \text{X}$ $r_a = k_a \left(C_{\text{Si}} C_v - \frac{\bar{C}_{\text{Si}}}{K_{\text{Si}}} \right)$ $(\bar{C}_{\text{Si}})_{\text{eq.}} = K_{\text{Si}} C_{\text{Si}} C_v$
Surface reaction	$\text{SiH}_4 \cdot \text{X} + 2\text{X} \longrightarrow \text{Si} \cdot \text{X} + 2\text{H}_2 \quad \text{X}$ $r_s = k_s \bar{C}_{\text{Si}} \left(\frac{C_v}{C_m} \right)^2$ $(\bar{C}_{\text{Si}})_{\text{eq.}} = 0$	$\text{SiH}_4 \cdot \text{X} + 4\text{X} \longrightarrow \text{Si} \cdot \text{X} + 4\text{H} \quad \text{X}$ $r_s = k_s \bar{C}_{\text{Si}} \left(\frac{C_v}{C_m} \right)^4$ $(\bar{C}_{\text{Si}})_{\text{eq.}} = 0$	$\text{SiH}_4 \cdot \text{X} \longrightarrow \text{Si} \cdot \text{X} + 2\text{H}_2$ $r_s = k_s \bar{C}_{\text{Si}}$ $(\bar{C}_{\text{Si}})_{\text{eq.}} = 0$
Desorption of hydrogen	$\text{H}_2 \cdot \text{X} \longrightarrow \text{H}_2(\text{g}) + \text{X}$ $r_d = -k_d' \left(C_v C_{\text{H}_2} - \frac{\bar{C}_{\text{H}_2}}{K_{\text{H}_2}} \right)$ $(\bar{C}_{\text{H}_2})_{\text{eq.}} = K_{\text{H}_2} C_v C_{\text{H}_2}$	$2\text{H} \cdot \text{X} \longrightarrow \text{H}_2(\text{g}) + 2\text{X}$ $r_d = \frac{-k_d'}{C_m} \left(C_{\text{H}_2} C_v^2 - \frac{\bar{C}_{\text{H}_2}^2}{K_{\text{H}_2}} \right)$ $(\bar{C}_{\text{H}_2})_{\text{eq.}} = K_{\text{H}_2} C_{\text{H}_2} C_v^2$	

Surface reaction controlling, with molecular hydrogen adsorption:

$$r_{hp} = \frac{k_s K_{Si} C_m}{(1 + K_{Si} C_{Si} + K_{H_2} C_{H_2})^3} C_{Si} \quad (11)$$

Hydrogen desorption controlling, with molecular hydrogen adsorption:

$$r_{hp} = \frac{k'_d C_m}{K_{H_2}} \quad (12)$$

Silane adsorption controlling, with atomic hydrogen adsorption:

$$r_{hp} = \frac{k_a C_m}{1 + \sqrt{K_h C_{H_2}}} C_{Si} \quad (13)$$

Surface reaction controlling, with atomic hydrogen adsorption:

$$r_{hp} = \frac{k_s K_{Si} C_m}{(1 + K_{Si} C_{Si} + \sqrt{K_h C_{H_2}})^5} C_{Si} \quad (14)$$

Hydrogen desorption controlling, with atomic hydrogen adsorption:

$$r_{hp} = \frac{k'_d C_m}{K_h} \quad (15)$$

Silane adsorption controlling, with no hydrogen adsorption:

$$r_{hp} = k_a C_m C_{Si} \quad (16)$$

Surface reaction controlling, with no hydrogen adsorption:

$$r_{hp} = \frac{k_s K_{Si} C_m}{1 + K_{Si} C_{Si}} C_{Si} \quad (17)$$

The overall rate of heterogeneous decomposition of silane can be described by one of the equations (10) - (17), depending on the controlling step. If adsorption, surface reaction and desorption are all important, then overall rate at steady state conditions is given by the relation:

$$r_0 = r_a = r_s = r_d$$

The concentrations of adsorbed silane, silicon and hydrogen can be evaluated from the three independent equations, implicit in the above relation. Thus the overall rate of heterogeneous pyrolysis of silane can be expressed in terms of gas phase concentrations and the equilibrium adsorption coefficients. The equilibrium adsorption coefficients can be evaluated from independent adsorption studies. Since the equilibrium adsorption constants and specific rate coefficients are all functions of temperature, a large amount of kinetic data at different temperatures will be necessary to evaluate all the equilibrium and rate constants from kinetic data alone. An example of this type of analysis is given by Hougen and Watson (Reference 1-1) for the hydrogenation of Codimer. As had been pointed out by many investigators, it may be extremely difficult, if not impossible, to determine the mechanism and identify the rate-limiting step from kinetic data alone. Experimental kinetic data may fit equally well to more than one overall rate expression, if all the equilibrium and rate constants are derived from the kinetic data. Thus it is very important to obtain the equilibrium adsorption constant from independent adsorption studies, if the rate equations are to be used with confidence in any modeling effort.

The kinetic parameters studies of activation energy and frequency for the overall heterogeneous pyrolysis of silane reported in the literature vary greatly. Joyce and Bradley (Reference 1-9) reported an activation energy of 37 kcal/mole for the epitaxial CVD of silicon on silicon substrates with substrate temperatures in the range of 920 - 1260°C. They indicated that mass transfer is the rate-limiting step in the temperature range of 1100 - 1260°C and that either chemisorption, surface reaction or desorption is the limiting step in the temperature range of 950 - 1100°C. Their experiments were carried out at low silane pressures (2 mm Hg) to suppress homogeneous decomposition. They speculated that surface reaction or desorption of hydrogen is the rate-limiting step in the low-temperature (950 - 1100°C) range. Henderson and Helm (Reference 1-8) reported an activation energy of 20 kcal/mole for the growth of homoepitaxial growth of silicon on silicon substrates using silane pyrolysis at temperatures of 823 - 983°C and pressures of 0.15 - 0.02 torr. From an analysis of their data they surmised that surface chemical reaction is the controlling step, silane is weakly adsorbed and hydrogen is not adsorbed. Farrow (Reference 1-7) reported an activation energy of 17 kcal/mole for CVD of silicon on silicon substrates and that his data agreed well with the reaction mechanism proposed by Henderson and Helm (Reference 1-8).

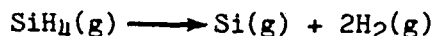
Everstiyn and Put (Reference 1-6) conducted the CVD of silicon on silicon substrates from the pyrolysis of silane at atmospheric pressure and a temperature range of 590 - 1050°C. They reported an activation

energy of 37 kcal/mole. The differences in the values of activation energy reported are generally attributed to impurities on the substrates and different surface orientations. The rate limiting step has not been established clearly in the literature. Experimental data at atmospheric pressure are also very limited. It therefore seems imperative to carry out an experimental program to (1) obtain kinetic data on the CVD of silicon from silane pyrolysis at atmospheric pressure and (2) establish the rate-limiting step for various experimental conditions.

SECTION VI

HOMOGENEOUS PYROLYSIS

Homogeneous decomposition of silane (step R₁ in Figure 2-1) is a simple first-order vapor phase pyrolysis of silane. The stoichiometric equation can be written as:



The rate of reaction r_h can be expressed as

$$r_h = - \frac{1}{V} \frac{dN_{\text{Si}}}{dt} = k_h C_{\text{Si}} \quad (18)$$

Joyce and Bradley (Reference 1-9) reported an activation energy of 51 kcal/mol. Eversteyn (Reference 1-5) reported a value of 30 kcal/mol after conducting extensive research on vapor phase pyrolysis of silane in the temperature range of 660 - 755°C. Eversteyn determined also the critical concentrations of silane necessary for homogeneous reaction in the temperature range 780 - 1136°C. This critical concentration decreased from a value of 0.248% at 780°C to a value of 0.002% at 1136°C. The logarithm of the critical concentration varies linearly with the inverse of the temperature with an activation energy of 38 kcal/mol. Joyce and Bradley (Reference 1-9) reported that homogeneous silane pyrolysis can be totally suppressed if the silane pressure is kept below 2 mm Hg.

SECTION VII

HOMOGENEOUS NUCLEATION

In the absence of all foreign materials and surface, vapor condensation is blocked by an activation free energy barrier which arises from surface free energy increases resulting from appearance of embryos of the more condensed phase. This can be seen more clearly through free energy considerations. In homogeneous nucleation processes (step R₂ in Figure 3-1) it is necessary to go to higher super saturations to get over the free energy barrier. The excess free energy of a vapor at a supersaturated pressure p over that of a liquid at the same temperature T is given by the relation

$$\Delta f = RT \ln (p/p')$$

where Δf is the excess free energy per gram, R is the gas constant per gram of vapor, and p' is the saturation vapor pressure at temperature T . This Δf will be the decrease in the system free energy as an embryonic droplet is formed. At the same time there will be a free energy increase associated with the embryo's surface free energy, which can be written as $(4/3)\pi r^3 \sigma$, where r is the radius of the embryo and σ is the specific surface free energy (ergs/cm²). The phase transition can occur only through drop-wise condensation (as all foreign materials are absent). Thus the free energy decrease by phase transition is dependent on the volume of the embryo and can be written as $(4/3)\pi r^3 \rho RT \ln S$, where ρ is the density of the condensed phase and S is the supersaturation ratio (p/p'). Thus the net free energy change for embryo formation can be shown to be

$$\Delta F = 4\pi r^2 \sigma - (4/3)\pi r^3 \rho RT \ln S \quad (19)$$

The free energy change has to be negative for successful vapor condensation. At supersaturation ratios of 1 and <1 ΔF is always positive and phase transfer does not occur. However, as S increases, ΔF goes through a maximum. This is the maximum free energy barrier (ΔF^*) to be surmounted for vapor condensation (Figure 7-1).

Invoking the basic principle that any process in which ΔF decreases is a spontaneous process, we can see that if, by any means, the embryo can reach the maximum ΔF , the slightest additional condensational growth of the embryo beyond the size associated with the maximum ΔF should lead to irreversible growth of the embryo from supersaturated vapor. Thus the radius of the embryo r for which ΔF attains its maximum will be a critical embryo radius for whatever S value present. This critical radius can be obtained by differentiating Eq. (19) with respect to r at constant T and S and setting the $\partial(\Delta F)/\partial r$ equal to zero and then solving for r^* (critical radius).

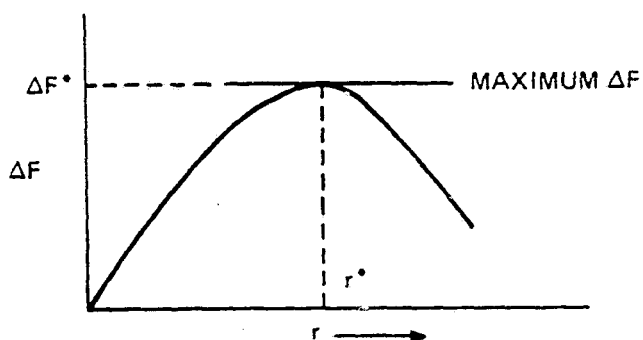


Figure 7-1. Free Energy of Formation of Critical Nuclei

$$r^* = 2\sigma / \rho RT \ln S \quad (20)$$

This r^* is the radius of the embryo that is essential for vapor condensation at temperature T and supersaturation S . Thus r^* is the smallest diameter of the condensed phase. The g^* , the number of molecules or atoms in an embryo of critical radius r^* , is given by the relation $((4/3)\pi r_p^3 = gm)$ where m is the mass of 1 molecule,

$$g^* = \frac{32\pi\sigma^3}{3m\rho^2 R^3 T^3 (\ln S)^3} \quad (21)$$

So far, consideration of the thermodynamic aspects of nucleation phenomena has created a paradox. The supersaturated vapor is in a metastable state because its specific free energy exceeds, by the finite amount, $RT \ln S$, that of condensed phase at the same temperature. However, it cannot jump to the preferred lower free energy state because that jump can only proceed via formation of tiny drops, beginning with clusters of two, three, four molecules, etc. The growth of such embryos of the new phase carries the system up to states where the total free energy of the system has risen more by creation of new surface free energy of the embryonic drops than it has fallen by virtue of the bulk free energy change accompanying the phase transition that produced these drops. That is, phase transition is always, in the homogeneous case, blocked by an activation energy barrier.

This barrier can be overcome only by raising S high enough, which will lower the ΔF^* and the r^* that must be exceeded in order that the system will spontaneously shift to the preferred condensed phase. Even at subsaturations ($S < 1$), there exists, as a steady-state population, a distribution of embryos satisfying a Boltzmann-type relation:

$$n_g = n_1 e^{-\Delta F_g / kT} \quad (22)$$

in which n_g is the number of clusters of g molecules and ΔF_g is in terms of ' g '; k is the Boltzmann constant. If rare fluctuation phenomena can, even at $S < 1$, support such a population of molecular clusters, then when S rises above unity, surely a general increase in that population is expected at all g . Thus, for some large S ($S \approx 5, 6$) it can be expected to reach a point where fluctuations can send some embryos over the top of the energy barrier whereupon the supercritical embryos can subsequently grow without limit until the vapor pressure is pulled from p down to p' and the system is thermodynamically stabilized. Substituting Eq. (20) for r^* in Eq. (19), the free energy barrier to be surmounted for the formation of critical embryos of size r^* is obtained:

$$\Delta F^* = \frac{16\pi \sigma^3}{3(\rho RT \ln S)^2} \quad (23)$$

Hirth and Pound (Reference 1-3) enumerated the classical nucleation theory of Volmer and Weber, in which the rate of nucleation is formulated in terms of equilibrium population critical embryos n_g , surface area of embryos A and an impingement frequency factor ω . Volmer and Weber's equation for homogeneous nucleation rate is

$$J = A \omega n_g^* \quad (24)$$

where $A = 4\pi r^{*2}$, $\omega = a_c p / (2\pi m k T)^{1/2}$ and n_g^* is given by Eq. (22). Substituting these expressions in Eq. (24), we obtain

$$J = a_c (4\pi r^{*2}) \left[\frac{p}{(2\pi m k T)^{1/2}} \right] n_1 e^{-\Delta F^*/kT} \quad (25)$$

where a_c is the condensation coefficient for molecules impinging on the critical embryos.

Hirth and Pound (Reference 1-3) also described a refinement of Volmer and Weber's theory by Becker and Doering and Zeldovich. In the refined treatment, instead of using equilibrium concentrations the actual steady-state concentrations of critical nuclei were calculated by considering the changes in cluster size by the addition and removal of a molecule. This elegant approach resulted in the incorporation of an additional term Z' , the so called nonequilibrium factor, into Eq. (24). The refined expression for homogeneous nucleation rate then becomes,

$$J = a_c Z' (4\pi r^{*2}) \left[\frac{p}{(2\pi m k T)^{1/2}} \right] n_1 \exp(-\Delta F^*/kT) \quad (26)$$

where

$$Z' = \frac{m (PRT \ln S)^2}{\rho \cdot 8 \pi \sigma (\sigma kT)^{1/2}}$$

Substituting Eq. (20) for r^* and noting that $p = nkT$, Eq. (26) can be simplified to yield

$$J = \left(\frac{a_c}{\rho} \right) \left(\frac{2\sigma m}{\pi} \right)^{1/2} \exp(-\Delta F^*/kT) n_1^2 \quad (27)$$

McDonald (Reference 7-1), in a similar treatment, considering the rate of growth and decay of critical embryos, arrived at a homogeneous nucleation rate expression identical to Eq. (27). The inherent fallacy in Eq. (27) arises from assigning macroscopic thermodynamic properties to microscopic embryos. Many corrections have been proposed in the literature to correct this problem. For this reason, for critical embryos in the size range $1 < g^* < 50$ a different statistical mechanical model should be used in place of Eq. (27). Lothe and Pound (Reference 7-2) suggested another correction factor to Eq. (27) to take into account the contributions of molecular entropy of mixing of small clusters with monomer, rotational and vibrational free energies of initial embryos to the free energy of formation of critical embryos. However, all these corrections can be taken care of by assigning a value sufficiently less than unity to the condensation coefficient a_c . Equation (27) is strictly applicable to nucleation of droplets from unary vapors. It had been reported in the literature that the same equation can be applied to nucleation of crystallites from both unary and binary vapor with proper modifications to a_c or effective supersaturation ratio.

SECTION VIII

HETEROGENEOUS NUCLEATION

Heterogeneous nucleation (step R_{10} in Figure 2-1) is the process by which the adsorbed silicon atoms on the substrate are incorporated in the silicon deposit. The thermodynamics of heterogeneous nucleation is very similar to that of homogeneous nucleation. The added parameter is the equilibrium contact angle of the nuclei. A schematic model of nucleation of a spherical cap-shaped nucleus on a solid substrate is shown in Figure 8-1.

The free energy of formation of a spherical cap-shaped nucleus consists of two terms: the bulk free energy change ΔF_b and surface free energy change ΔF_s .

$$\Delta F_b = \frac{4}{3}\pi r^3 X(\theta) \Delta f \quad (28)$$

$$\Delta f = -pRT \ln S \quad (29)$$

$$X(\theta) = \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4} \quad (30)$$

where $X(\theta)$ is a geometric factor relating the volume of a spherical cap to that of a sphere of radius r , and θ is the equilibrium contact angle determined by the surface free energy equilibrium.

$$\sigma_{s-v} = \sigma_{c-s} + \sigma_{c-v} \cos \theta \quad (31)$$

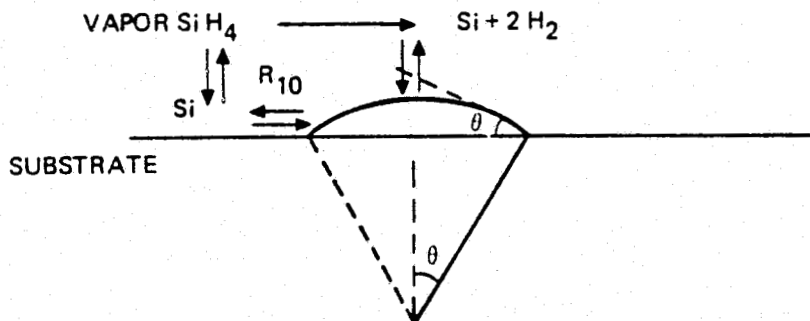


Figure 8-1. Spherical Cap-Shaped Nucleus

and where σ_{s-v} , σ_{c-s} and σ_{c-v} are the specific interfacial free energies of the substrate vapor, condensate-substrate, and condensate-vapor interfacing, respectively. The surface free energy term is given by

$$\Delta F_s = 4\pi r^2 X(\theta) \sigma \quad (32)$$

Therefore, the total free energy change associated with the formation of nuclei is

$$\Delta F = 4\pi r^2 X(\theta) \sigma - \frac{4}{3} \pi r^3 X(\theta) \rho RT \ln S \quad (33)$$

The variation of the free energy change with r is very similar to that for the homogeneous nucleation, as shown in Figure 7-1, and passes through a maximum corresponding to the critical nuclei radius r^* . The value of this r^* can be found by maximizing ΔF with respect to r , and r^* is found to be:

$$r^* = \frac{2\sigma}{\rho RT \ln S} \quad (34)$$

and

$$\Delta F^* = \frac{16}{3} \frac{\pi \sigma^3 X(\theta)}{(\rho RT \ln S)^2} \quad (35)$$

By comparing Eqs. (34) and (35) with Eqs. (20) and (23), it can be readily observed that the radius of critical nucleus is the same in both homogeneous and heterogeneous cases, but the critical free energy change in the heterogeneous case is dependent on the contact angle θ . If the contact angle θ is zero ($X(\theta) = 0$, complete wetting of the substrate by the condensate), ΔF^* is zero and nucleation is most rapid. If θ is equal to 180 deg, corresponding to no wetting of wall at all, $X(\theta) = 1$ and Eq. (35) reduces to Eq. (23), the expression for homogeneous nucleation. This is the limiting case in which the substrate has negligible potency as a nucleation catalyst.

Heterogeneous nucleation kinetics are formulated much the same way as homogeneous nucleation kinetics and the rate of nucleation is given by

$$J = Z' \omega n^* \quad (36)$$

where n^* is the equilibrium concentration of critical nuclei, ω is the frequency with which a single atom joins a critical nucleus and Z' is a nonequilibrium (Zeldovich) factor to account for the steady-state

growth or decay of clusters by addition and removal of single atoms. The addition of single atoms to critical nucleus can occur either by direct adsorption from vapor or by surface diffusion of adsorbed atoms. However, it is believed that the surface diffusion is the more predominant process.

Hirth and Pound (Reference 1-3) cite the work of Pound et al., which shows that surface diffusion proceeds more rapidly than direct adsorption from vapor by a factor of

$$\exp [(\Delta F_{des}^* - F_{sd}^*)/kT]$$

Therefore, based on the premise that surface diffusion is the predominant process, ω is given by the expression:

$$\omega = \bar{C}_s 2\pi r^* a \sin \theta \cdot \bar{\omega} \exp\left(\frac{-\Delta F_{sd}^*}{kT}\right) \quad (37)$$

where $(\bar{C}_s 2\pi r^* a \sin \theta)$ is the probability that an adatom is adjacent to a critical embryo and

$$\left\{ \bar{\omega} \exp\left(\frac{-\Delta F_{sd}^*}{kT}\right) \right\}$$

is a frequency with which an adjacent adatom will jump to join a critical nucleus. The nonequilibrium correction for the case of heterogeneous nucleation on a substrate is given by:

$$Z = \left(\frac{\Delta F^*}{3\pi kT g^* 2} \right)^{1/2} \quad (38)$$

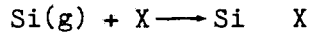
$$n^* = \bar{C}_s \exp\left(\frac{-\Delta F^*}{kT}\right) \quad (39)$$

and substituting Eqs. (37), (38) and (39) in Eq. (36) and simplifying, we obtain:

$$J = \frac{ma \sin \theta \bar{\omega} RT \ln S}{2(\sigma kT/X(\theta))^{1/2}} \exp\left\{ \frac{(-\Delta F_{sd}^* - \Delta F^*)}{kT} \right\} \bar{C}_s^2 \quad (40)$$

In Eq. (40), \bar{C}_s is the concentration of adsorbed silicon concentration. Referring to Figure 2-1, silicon may be adsorbed either from vapor phase (step R₇) or through the decomposition of silane on the substrate (step R₉). Thus the concentration of adsorbed silicon will be determined either by the adsorption-desorption rates of silicon or by the heterogeneous pyrolysis of silane.

For the adsorption of silicon:



$$r_a = k_a C_s C_v - k'_a \bar{C}_s$$

$$= k_a \left[C_s C_v - \frac{C_s}{K_s} \right]$$

at equilibrium, $r_a = 0$ and $\bar{C}_s = k_s C_s C_v$. If silicon is deposited through pyrolysis of silane, the concentration of adsorbed silicon will be equal to the concentration of silane molecules reacted.

$$\bar{C}_s = \bar{C}_m - \bar{C}_v - \bar{C}_{si} - \bar{C}_h$$

If the adsorption of silane, reaction of silane and desorption of hydrogen are all at equilibrium,

$$\bar{C}_{si} = 0, \bar{C}_h = K_{h2} C_v C_{h2} \text{ (molecular hydrogen adsorption)}$$

$$= \sqrt{K_h} C_v \sqrt{C_{h2}} \text{ (atomic hydrogen adsorption)}$$

$$= 0 \text{ (no hydrogen adsorption)}$$

SECTION IX

CRYSTAL GROWTH

The mechanism of crystal growth consists of adsorption of monomer onto a low-index facet, surface diffusion to a ledge, association to the ledge, diffusion along the ledge, and incorporation into the crystal at a kink site. In crystal growth, ledges may be formed when two nucleated crystallites impinge upon one another or when a crystallite is nucleated in a substrate. The ideal growth rate J_c will be given by the difference between gross flux incident on the growing surface $f_p/(2\pi MRT)^{1/2}$ and the gross reevaporation flux $f_p'/(2\pi MRT)^{1/2}$. Deviations from ideality are accounted for by introduction of a condensation coefficient a_c . Thus the growth rate is given by the modified Hertz-Knudsen equation

$$J_c = \frac{a_c f(p - p')}{(2\pi MRT_s)^{1/2}} \quad (41)$$

The growth kinetics will now be described for three different cases in which silicon adatoms are generated by (1) direct adsorption of silicon from vapor phase (step R_7), (2) dissociation of adsorbed silane (step R_9), or (3) dissociation of silane at ledges (step R_5).

A. DIRECT ADSORPTION FROM VAPOR PHASE

In this case, the continuity equation for adsorbed silicon is given by

$$\left[\frac{f_p}{(2\pi MRT_s)^{1/2}} \right] - \left[N_s \exp\left(\frac{-\Delta F_{des}}{RT}\right) \right] = D_s \frac{\partial^2 N_s}{\partial x^2} \quad (42)$$

and the condensation coefficient a_c is

$$a_c = \frac{\bar{N}_s}{N_{se}} = \frac{\sqrt{2} \bar{X}}{\lambda} \tanh \frac{\bar{\lambda}}{\sqrt{2} \bar{X}} \quad (43)$$

where N_s and N_{se} are the average and equilibrium concentrations of adsorbed silicon, λ is the mean spacing between ledges, and X is the rms distance that an adsorbed silicon may diffuse before reevaporating, and given by

$$\bar{X} = \sqrt{2} a \exp\left(\frac{\Delta F_{des} - \Delta F_{sd}}{2RT}\right) \quad (44)$$

At low supersaturations $\bar{\lambda}$ is given by

$$\bar{\lambda} = \frac{19\sigma\Omega}{RT_s} \ln \frac{p}{p'} \quad (45)$$

At higher supersaturations, above a critical pressure p' given in Eq. (45) with $\bar{\lambda} = 3\sqrt{2}\bar{X}$, λ is given by

$$\bar{\lambda} = 3\sqrt{2}\bar{X} \quad (46)$$

At still higher supersaturation the nucleation of adsorbed silicon becomes so rapid that $\bar{\lambda} \ll \bar{X}$ and a_c becomes unity. Therefore, substituting the proper expression for $\bar{\lambda}$ and Eq. (43) in Eq. (42) will yield the expression for growth rate.

B. DISSOCIATION OF ADSORBED SILANE

For this case, Eq. (42) will be replaced by:

$$N_{si}r_s - N_s \nu \exp\left(\frac{-\Delta F_{des}}{RT_s}\right) = \left(D_s \frac{\partial^2 N_s}{\partial x^2}\right) \quad (47)$$

Where N_{si} is the concentration of adsorbed silane and r_s is the rate coefficient for silane decomposition.

$$J_c = a_c N_{si} r_s - \frac{fp'}{(2\pi MRT_s)^{1/2}} \quad (48)$$

a_c is still determined by Eq. (43), but (p/p') should be replaced by equivalent supersaturation ratio for this case.

C. DISSOCIATION OF SILANE AT LEDGES

In this case the silicon atoms produced from dissociation of silane are directly incorporated in the crystal, and Eq. (42) will be replaced by

$$f p_{si} (2\pi MRT)^{-1/2} - N_{si} \nu \exp\left(\frac{-\Delta F_{des}}{RT}\right) = D_s \frac{\partial^2 N_s}{\partial x^2} \quad (49)$$

In this equation ΔF_{des} , M , and D_S refer to properties of silane. Equations (41) or (43) still determine the growth rate with $\bar{\lambda}$ referring to the diffusion distance for adsorbed silane.

SECTION X

GLOBAL RATE OF SILICON CVD (CONCLUSIONS)

Rate expressions for the individual steps involved in the chemical vapor deposition of silicon have been developed. These equations can be useful in two distinct areas. If the exact mechanism of silicon CVD and the numerical values of all the coefficients and constants involved in the appropriate rate equation are known, the global rate of silicon CVD can be determined. The rate-limiting step or steps can also be determined from this information. Alternatively, the rate expressions can be used to evaluate the constants, determine the rate-limiting steps and formulate the mechanism of silicon CVD from experimental kinetic data on silicon CVD. The first area is modeling and simulation of the silicon CVD process, and the second area is basic research to determine the mechanism of silicon CVD.

It is essential to know the exact mechanism of the CVD process to derive the global rate of silicon CVD. Published literature does not make it clear as to the mechanism. Any mechanism of silicon CVD shall consist of four basic steps: (1) mass transport of silane, (2) pyrolysis of silane, (3) nucleation of silicon, and (4) crystal growth. Rate of mass transport is uniquely given by Eq. 7. The mass transfer coefficient is a function of flow conditions and reactor geometry. Empirical correlations are available to evaluate the mass transfer coefficient for many different reactors. Mass transport is reported to be the limiting step in silicon CVD at temperatures above 1050°C. Pyrolysis of silane and nucleation of silicon are reported to occur by homogeneous and heterogeneous processes. The heterogeneous process, however, is believed to be the dominant process in silicon CVD. Reported literature indicates that surface reaction (Eq. 11) is the rate-limiting step in heterogeneous pyrolysis. Heterogeneous nucleation rate is given by Eq. (40). Crystal growth for the heterogeneous process can occur either through dissociation of silane molecules adsorbed on ledges (Eq. 49) or through surface diffusion of adsorbed silicon atoms to ledges (Eq. 48). It is generally believed that growth by surface diffusion is the more predominant process.

For the homogeneous process, the pyrolysis of silane is given by Eq. (18); the nucleation is given by Eq. (27), and crystal growth is given by Eq. (42). Thus we have two competing mechanisms, homogeneous and heterogeneous, for the chemical vapor deposition of silicon. These mechanisms should not be construed as real mechanisms of silicon CVD but only as examples to illustrate the derivation of global rate of silicon CVD.

Consider the heterogeneous mechanism. The four steps involved in this mechanism are (1) mass transport of silane, described by rate expression (Eq. 7), (2) heterogeneous pyrolysis with surface relation as the rate-limiting step (Eq. 11), (3) heterogeneous nucleation (Eq. 40), and (4) crystal growth by surface diffusion of adsorbed silicon (Eq. 48). The rates of these four steps can now be calculated for given bulk vapor phase concentrations of silane and hydrogen, temperatures of substrate

and vapor phase, and reactor pressure. Numerical values of various coefficients and constants are either to be taken as reported in the literature or estimated. Experimental data on nucleation and growth are lacking. If one of the steps is particularly slow (e.g., by an order of magnitude), that can be designated as the rate-limiting step and the remaining three steps can be assumed to occur at equilibrium conditions (i.e., highest possible rates). The rate of the limiting step will then be the global rate. For details of this type of analysis one should refer to Smith (Reference 1-2) or Hougen and Watson (Reference 1-2). This is the same type of procedure we followed in deriving overall rate equations for heterogeneous pyrolysis of silane. Thus the two basic elements needed to use the rate expressions derived in this report to formulate the global rate of silicon CVD are (1) the exact mechanism of silicon CVD and (2) numerical values for the various constants involved in the rate expressions. The rate expressions will also be useful in analyzing experimental data on mass transport of silane, pyrolysis of silane and nucleation and growth of silicon crystals.

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